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AB 26

NITROSAMINES

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INTRODUCTION

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Titles of the FABs now available are given on the back cover of this booklet. For up-to-date lists of FABs or suggestions for new topics please write to the address on the back cover. New subjects are searched for at least the five most recent volumes of Food Science and Technology Abstracts. Thereafter each FAB is updated monthly. Copies of each month's abstracts on any topic may be obtained as indicated on the back cover of this publication. At the end of each volume of up-dating, the abstracts are merged and made available as a separate supplement to the original FAB.

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Copies of all original articles referred to in the abstracts may be bought (or occasionally borrowed) from the International Food Information Service. A form for ordering these is provided at the end of this FAB.

Coverage of the subject has been restricted to that of Food Science and Technology Abstracts, which covers over 1200 of the important food journals, patents from 20 countries and books published world-wide. Every effort is made to include all significant references, but editorial discretion is used on the many articles of borderline interest. If the reader particularly needs an exhaustive search of the subject, we will be pleased to provide any other references that we have available. We would, in any case, encourage readers to write or telephone us with any comments or queries that they may have.

H. BROOKES

EDITOR

1

Determination of volatile N-nitroso compounds in various samples of edible vegetable oils and margarine (commercially available products).

Hedler, L.; Schurr, C.; Marquardt, P.

Journal of the American Oil Chemists' Society 56 (7) 681-684 (1979) [4 ref. En] [Pharmakologisches Inst. der Univ., Hermann-Herder-Strasse 5, D-78 Freiburg 1, Federal Republic of Germany]

Examination of samples of various commercially available vegetable oils (olive oil, sunflower oil, thistle oil, linseed oil, plant germ oil, etc.) and of various samples of margarine for the presence of volatile N-nitroso-compounds yielded the following results. By means of the following procedure (GLC, alkaliflame ionization detector GLC, thermal energy analyser), N-nitrosodimethylamine (NDMA) was found to be present in 21 of 61 different samples of vegetable oil, in concn. ranging from $< 1 \mu\text{g/kg}$ to $23 \mu\text{g/kg}$. 18 samples contained N-nitrosodiethylamine (NDEA) in concn. varying between $< 1 \mu\text{g/kg}$ and $27.8 \mu\text{g/kg}$. 37 out of 107 different samples of margarine were shown to contain N-nitroso compounds. NDMA was found to be present in 15 samples. The range of concn. determined was between $< 1 \mu\text{g/kg}$ and $5.8 \mu\text{g/kg}$. 33 samples contained NDMA in concn. varying between $< 1 \mu\text{g/kg}$ and $7.5 \mu\text{g/kg}$. AS

2

The transnitrosation of secondary amines S-nitrosocysteine in relation to N-nitrosamine formation in cured meats.

Dennis, M. J.; Davies, R.; McWeeny, D. J.

Journal of the Science of Food and Agriculture 30 (6) 639-645 (1979) [23 ref. En] [Min. of Agric., Fisheries & Food, Food Lab., Haldin House, Queen Street, Norwich UK]

The reactions at 37°C of S-nitrosocysteine hydrochloride with 3 secondary amines, N-methylaniline, morpholine and pyrrolidine, were studied at pH 2.65, 5.5 and 9.75. The reactions result in the formation of the N-nitroso derivatives of the 3 amines at all 3 pH values studied. The rates of N-nitrosation and final yields of products in these reactions were compared with those in reactions in which the N-nitrosation of the secondary amines was effected by nitrite. The comparative rates varied considerably according to the amine being studied and the reaction pH. The relevance of these findings to nitrosamine formation in cured meat and in vivo are discussed. Reaction of S-nitrosocysteine hydrochloride with all amines at pH 9.75 and with N-methylaniline at pH 5.5 resulted in some N-nitrosamine formation in the headspace above the reaction mixture. The stability of S-nitrosocysteine hydrochloride was studied as a function of pH. The compound was fairly stable at pH 2.65, but decomposed rapidly at pH 5.5 and 9.75. The decomposition reaction at pH 5.5 followed three-halves order kinetics, but that at pH 9.75 did not conform to simple kinetics. AS

3

Nitrosamine reduction.
Unilever Ltd.

British Patent 1 537 334 (1979) [En]

Nitrite-cured meat products are treated with 6-alkoxy-1,2-dihydroquinolines to reduce the formation of nitrosamines. IFT

4

Effect of pork belly composition and nitrite level on nitrosamine formation in fried bacon.

Pensabene, J. W.; Feinberg, J. I.; Dooley, C. J.; Phillips, J. G.; Fiddler, W.

Journal of Agricultural and Food Chemistry 27 (4) 842-845 (1979) [25 ref. En] [E. Regional Res. Cent., Fed. Res. Sci. & Education Administration, USDA, Philadelphia, Pennsylvania 19118, USA]

A study was conducted to determine the effect of compositional factors (fat, moisture, protein) on nitrosamine formation in bacon prepared from matched pairs of pork bellies cut into thirds. The compositional factors varied significantly ($p = 0.05$) from section to section within the same side but did not vary from side to side within the same section of matched pair. Both N-nitrosopyrrolidine and N-nitrosodimethylamine were most highly correlated with residual and added nitrite and to a lesser degree with the compositional factors. AS

5

Consumer confusion.

Francis, F. J.

Journal of Food Protection 42 (8) 679-682 (1979)

[34 ref. En] [Dep. of Food Sci. & Nutr., Univ. of Massachusetts, Amherst, Massachusetts 01003, USA]

Some possible causes of popular lack of understanding of food-related topics are identified and discussed. 2 such causes, deliberate dissemination of misinformation, and provision of information for which there has been no generally articulated requirement, are briefly considered. A 3rd cause, complexity of technical concepts such as estimation of degree of risk in food safety is discussed in greater detail and literature on carcinogenicity and risk/benefit evaluation is reviewed. It is pointed out that it is important to separate risks derived from epidemiological data (real risks) from risks derived by extrapolation from animal tests (estimated risks). Responsibility for determining at what level a risk is unacceptable is a controversial issue. DIH

6

Nitrite-lipid reaction in aqueous system: inhibitory effects on N-nitrosamine formation.

Kurechi, T.; Kikugawa, K.

Journal of Food Science 44 (5) 1263-1266, 1271 (1979) [24 ref. En] [Tokyo Coll. of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan]

The chemical interaction of lipids and lipid-containing foods with nitrite in a mild acidic aqueous system was investigated. Methyl linoleate-coated silica gel, Intralipid [an emulsion containing soybean oil and yolk lecithin], cows' milk, mayonnaise, yolk and miso reduced a considerable amount of nitrite. Methyl linoleate-coated silica gel and cows' milk extensively prevented the formation of carcinogenic N-

nitrosamines. It seemed likely that the unsaturated fatty acid residues were responsible for the interaction of lipids with nitrite. Methyl linoleate was changed into two or more unidentified products, neither of which was the hydroperoxides of the ester. IFT

7

Characterization of pyrolysis conditions and interference by other compounds in the chemiluminescence detection of nitrosamines.

Hansen, T. J.; Archer, M. C.; Tannenbaum, S. R. *Analytical Chemistry* 51 (9) 1526-1528 (1979) [24 ref. En] [Dep. of Nutr. & Food Sci., Massachusetts Inst. of Tech., Cambridge, Massachusetts 02139, USA]

During studies on the interaction of food materials with nitrous acid, a method was required for distinguishing nitrosamines from other materials that give a response in a thermal energy analyser chemiluminescence detector. Response of one such detector as a function of pyrolysis chamber temp. has been characterized for several nitrosamines and for an aliphatic C-nitro compound, an aromatic C-nitro compound, a nitramine, an alkyl nitrite, and a nitroso urea. The response-temp. profiles are valuable in distinguishing among the various compounds and in optimizing the sensitivity of the detector for use in chromatography. Other tests, including photolysis and stability toward nitrite-scavenging reagents, further aid in distinguishing among the various compounds. AL

8

N-nitrosation by solid sodium nitrite. Promotion by halocarbon solvents and inhibition by ascorbic acid. Roller, P. P.; Uhm, S. J.; Slavin, B. W.; Keefer, L. K. *Abstracts of Papers, American Chemical Society* 177 (1) AGFD 32 (1979) [En] [Analytical Chem. Section, Lab. of Carcinogen Metabolism, National Cancer Inst., NIH, 37/IE-22, Bethesda, Maryland 20014, USA]

Halocarbons are important industrial solvents and analytical reagents used for extraction of foodstuffs, natural products, and environmental samples. Certain halocarbon solvents react efficiently with secondary amines dissolved in them, giving intermediates which, in the presence of insoluble nitrite, yield N-nitroso compounds. Typically, 0.0024M pyrrolidine and 4-fold molar excess of NaNO_2 in CH_2Cl_2 produced a 50% yield of N-nitrosopyrrolidine after 4.25 days at 25°C. The nitrosamine yield varied with the structure of the starting amine in the order pyrrolidine > piperidine > diethylamine and with the solvent in the order CH_2BrCl > CH_2Cl_2 > $\text{ClCH}_2\text{CH}_2\text{Cl}$ > CF_2Cl_2 > $\text{CCl}_4 \approx \text{CHCl}_3$. With dihalomethanes, the primary nitrosamine-forming mechanism appears to involve initial reaction of solvent with amine, to produce formaldiminium ions ($\text{CH}_2 = \text{NR}_2^+ \text{Cl}^-$), which then react efficiently with nitrite ion, ultimately rearranging to the observed product. The postulated intermediate was also trapped with other nucleophiles, such as cyanide ion or excess amine. Ascorbic acid, potassium iodide and potassium carbonate were found to partially inhibit the overall nitrosation reaction. Possible mechanisms of the inhibitory reactions and the significance of the findings in environmental carcinogenesis will be discussed. AS

9

Nitrite and nitrosamine update. (In 'Proceedings of the 31st Annual Reciprocal Meat Conference' (see FSTA (1980) 12 2S230)) [Lecture]

Wasserman, A. E.

pp. 121-128 (1979) [En] [E. Reg. Res. Cent., Fed. Res., Sci. & Education Administration, USDA, 600 East Mermaid Lane, Philadelphia, Pennsylvania 19118, USA]

Aspects discussed include: analytical techniques; nitrosamine concn. in foods; nitrosamines in non-food sources; possible in-vivo formation of nitrosamines from nitrites and amines; human and animal studies on formation of nitrosamines in the digestive tract; the current legal status of use of nitrite in cured meat products; possible substitutes for nitrite in cured meat products (with special reference to control of *Clostridium botulinum*); nitrosation inhibitors; carcinogenicity of nitrosamines; and possible consequences of banning nitrites. AJDW

10

Determination of volatile nitrosamines in crops and soils treated with dinitroaniline herbicides.

West, S. D.; Day, E. W., Jr.

Journal of Agricultural and Food Chemistry 27 (5) 1075-1080 (1979) [24 ref. En] [Lilly Res. Lab., Div. of Eli Lilly & Co., Greenfield, Indiana 46140, USA]

Volatile nitrosamines have been reported to be contaminants in several dinitroaniline herbicides. Since these nitrosamines are known to be carcinogenic in laboratory animals, it became necessary to analyse crops and soils treated with these herbicides for the presence of nitrosamines residues. In the procedures described, plant tissue was extracted with methanol, and soil was extracted with methanol/water (3:1). Sample extracts were purified by liquid-liquid extraction and alumina column chromatography. Measurement was accomplished by means of a gas chromatograph-thermal energy analyser. The sensitivity of the method was 0.2, 0.05, and 0.01 parts/billion for N-nitrosodi-n-propylamine in crops, soil, and water, resp. No detectable nitrosamine residues were observed in any crops [soybeans, carrots, cauliflower, lettuce, peanuts] treated with the herbicides trifluralin, benefin, or oryzalin. AS

11

Contamination of beer with trace quantities of N-nitrosodimethylamine.

Spiegelhalter, B.; Eisenbrand, G.; Preussmann, R.

Food and Cosmetics Toxicology 17 (1) 29-31 (1979) [5 ref. En] [Inst. für Toxikologie & Chemotherapie am Deutschen Krebsforschungszentrum, Heidelberg, Federal Republic of Germany]

Samples of bottled or canned beers were obtained in retail shops and supermarkets in Heidelberg between Oct. 1977 and April 1978, and draft beer was obtained directly from the tap and transferred to glass vessels. Chemiluminescence detection was used to analyse the 158 samples for contamination with volatile nitrosamines. Of these samples, 111 (70%) were found to contain N-nitrosodimethylamine (NDMA), the mean concn. being 2.7 p.p.b. and the max. level 68 p.p.b.

Numbers of samples with NDMA concn. p.p.b. (<0.5 , $0.5-1.4$, $1.5-4.9$ and ≥ 5.0) and mean and max. concn. resp. were: Pilsen lager, 21, 17, 9, 2, 1.2, 6.5; pale Export lager, 8, 9, 9, 1, 1.2, 6.5; top fermented pale ales, 7, 1, -, -, 0.2, 0.5; pale strong lager beer, 5, 6, 10, 2, 2.0, 5.0; top fermented dark ales, 2, 4, 6, 1, 2.4, 9.5; dark lager and dark strong lager beers, -, 4, -, 4, 11.2, 47; alcohol-free lager beers, 2, 2, 2, -, 1.6, 4.0; and special types of beer, 2, 11, 5, 6, 6.8 and 68. *N*-nitrosodiethylamine, the only other volatile nitrosamine found, was detectable in only 2 samples (at 0.5 and 3.0 p.p.b.). Samples with a nitrosamine content >3 p.p.b. were confirmed by high-resolution MS. VJG

12

Identification of nitrohexane in corn treated with nitrous acid.

Hansen, T. J.; Archer, M. C.; Tannenbaum, S. R. *Journal of Agricultural and Food Chemistry* 27 (5) 1072-1075 (1979) [24 ref. En] [Dep. of Nutr. & Food Sci., Massachusetts Inst. of Tech., Cambridge, Massachusetts 02139, USA]

Yellow corn was nitrosated with aqueous NaNO_2/HCl at pH 3 and a distillate of the reaction mixture was analysed by GLC-thermal energy analysis. A major peak was present in chromatograms of 3 different yellow corn samples, and the compound corresponding to this peak was purified by HPLC and identified by MS and GLC as nitrohexane, which was formed at a yield of 5-10 mg/kg corn. White corn contained no nitrohexane on nitrosation. Consequences of gastric nitrosation of corn in individuals having high levels of nitrite in gastric juice are discussed with reference to incidence of stomach cancer. It is also pointed out that nitroalkanes may interfere with thermal energy analyser detection of *N*-nitrosamines in foods; use of UV photolysis as an auxiliary method would distinguish between these 2 classes of compounds - nitrosamines are destroyed by long wavelength UV. DIH

13

[The effect of manufacturing methods and additives on the *N*-nitrosamine contents of cured meat products.] Über den Einfluss verschiedener Herstellungsverfahren und Zusätze auf den *N*-Nitrosamingehalt in gepökelten Fleischerzeugnissen. Mirna, A.; Spiegelhalder, B.; Eisenbrand, G. *Fleischwirtschaft* 59 (4) 553-556 (1979) [10 ref. De, en] [Bundesanstalt für Fleischforschung, 8650 Kulmbach, Federal Republic of Germany]

The effects of varying additions of nitrite curing salt (NPS), sodium ascorbate (NaASC), glucono- δ -lactone (GDL), sorbic acid (SS), blood or complex nitrosyl compounds (sodium pentacyano nitrosyl ferrate, SPNF) on the formation of *N*-nitrosamines (NAM) were investigated. NAM levels found in samples of canned Brühwurst and in dry sausages were generally at the limits of detection (around $0.5 \mu\text{g/kg}$); effects of various additives and manufacturing methods could therefore not be reliably determined. Dimethyl nitrosamine (NDMA) was found in most of the samples, and nitrosopyrrolidine (NPYR) in occasional dry sausage

samples. On average, dry sausages had higher NAM contents than Brühwurst. Increased NPYR were observed with increasing connective tissue contents. Residual NO_2^- content was reduced and NO_3^- increased by addition of NaASC or blood (haemoglobin). A drop in NAM formation may be expected when adding NaASC. Under the experimental conditions used NAM contents were generally too low to allow detection of a further effect of NaASC. GDL and SS had no effect on NAM production. [From En summ.] RM

14

International activities in the field of food additives, with particular reference to carcinogenicity.

Lu, F. C.

Ecotoxicology and Environmental Safety 4 (2) 301-309 (1979) [21 ref. En] [Food Additives Unit, WHO, Geneva, Switzerland]

The United States Food and Drug Administration has restricted and suspended the use of a number of food additives e.g. cyclamates, amaranth and saccharin, which had been generally recognised as safe, but were then reported to be carcinogenic to experimental animals. A brief review is given of the events leading up to these decisions, an outline of the 'Regulations' in certain major countries, as well as the recommendations of the WHO/FAO Expert Committee on Food Additives. VJG

15

[Nitrosamines and foods.] Nitrosamine und Lebensmittel. [Review]

Anon.

Schlachten und Vermarkten 78 (8) 242-245 (1979) [20 ref. De, en, fr]

This review discusses the carcinogenic properties of nitrosamines, their formation (role of NO_2^- , NO_3^- and amines), presence of nitrosamines in foods, reduction of NO_2^- in meat curing salt, and health hazards under existing food habits. Comprehensive studies in the USA suggest no cancer risk during normal lifespan. RM

16

[Hygienic studies on *N*-nitroso compounds. I. Survey of meat and fish meat products for volatile *N*-nitroso compounds.]

Maki, T.; Tamura, Y.; Shimamura, Y.; Nishigaki, S.; Naoi, Y.

Annual Report of Tokyo Metropolitan Research Laboratory of Public Health 28 (1) 145-148 (1977) [19 ref. Ja, en] [Tokyo Metropolitan Res. Lab. of Public Health, 24-1, Hyakunincho 3 chome, Shinjuku-ku, Tokyo, 160 Japan]

A total of 64 meat and fish products (hams, sausages, bacon) was examined for presence of dimethylnitrosamine (DMN) and diethylnitrosamine (DEN) by GLC with alkali flame ionization detection. No DMN or DEN was detected in any sample using this method with a level of detection of 1 part/billion. 8 of the samples were analysed using GLC with thermal energy detection; DMN was not detectable in

hamburger and was present in roasted ham and fish sausages at 0.06–0.60 parts/billion. DEN was not detectable in any of the 8 samples using this 2nd method. Nitrite content was measured in 16 of the samples and was in the range 1–10 p.p.m. [From En summ.] DIH

17

Interaction of wheat bran with nitrosamines and with amines during nitrosation.

Wishnok, J. S.; Richardson, D. P.

Journal of Agricultural and Food Chemistry 27 (5) 1132–1134 (1979) [20 ref. En] [Dep. of Nutr. & Food Sci., Massachusetts Inst. of Tech., Cambridge, Massachusetts 02139, USA]

Effects of addition of wheat bran to nitrosamine solutions on nitrosamine recovery and effects of presence of wheat bran on the nitrosation reaction were studied. For studies of binding to wheat bran, 200 mg wheat bran (obtained from American Association of Cereal Chemists, no further details given) was added to 10 ml of nitrosamine solution (0.5–0.7 $\mu\text{mol/ml}$) and effect on GLC recoveries from solution were compared with controls. 67% of control levels of *N*-nitrosodibutylamine was recovered from the bran treated sample; recoveries (as % controls) for *N*-nitrosodipropylamine (NDPA), *N*-nitropyrrolidine (NP) and *N*-nitrosomorpholine (NM) were 93–94%. Wheat bran was added to nitrosation reaction systems containing NaNO_2/HCl and dipropylamine, morpholine or pyrrolidine. Wheat bran increased rate of formation of NDPA, no NP was detected in presence or absence of wheat bran and wheat bran had no effect on formation of NM. Consequences of interactions of wheat bran with pre-existing or forming nitrosamines are discussed. DIH

18

Occurrence and determination of *N*-nitrosoproline and *N*-nitrosopyrrolidine in cured meat products.

Pensabene, J. W.; Feinberg, J. I.; Piotrowski, E. G.; Fiddler, W.

Journal of Food Science 44 (6) 1700–1702 (1979) [En] [USDA E. Reg. Res. Cent., SEA-AR, 600 E. Mermaid Lane, Philadelphia, Pennsylvania 19118, USA]

N-Nitrosopyrrolidine (NPYR) has been detected and confirmed at the ng/g level in a significant number of fried bacon samples. *N*-Nitrosoproline (NPRO) has been assumed to be the primary precursor of NPYR, but there are conflicting reports about its precise role. A method was developed for determining NPRO and a survey of 60 cured meat samples was conducted. No NPRO was detected in uncooked, conventionally cured bacon, Canadian bacon, ham, salt pork, pork roll or pastrami. NPRO was detected and confirmed in 1 of 7 dry cured bacon samples (106 ng/g), 8 of 12 dry cured ham samples (18–604 ng/g), and 5 of 6 samples of pork side meat (86–411 ng/g). The results suggest that NPRO may not be the main precursor of NPYR in bacon, but may have a role nitrosamine formation in dry-cured products. IFT

19

[Effects of recent research results on the nitrate/nitrite/nitrosamine problem in meat products.] Welche Konsequenzen ergeben sich für Fleischerzeugnisse aus den bisherigen Ergebnissen zum Nitrat/Nitrit/Nitrosamin-Problem? [Review]

Leistner, L.

Fleischwirtschaft 59 (10) 1415, 1416, 1418–1422, 1425–1427 (1979) [many ref. De] [Bundesanstalt für Fleischforschung, 8650 Kulmbach, Federal Republic of Germany]

In answer to a reader's enquiry, recent research on effect of $\text{NO}_2^-/\text{NO}_3^-$ additions to meat products is reviewed with reference to formation of carcinogenic nitrosamines, and inhibition of *Clostridium botulinum*. Attention is also given to the high contribution of vegetable products (especially from high N fertilization) and beer (64% of total intake for German male adults, vs. 10% from cured meats), and to endogenously produced NO_2^- (about 15% of daily load in saliva, 82% formed by intestinal flora). There is at present no practical substitute for $\text{NO}_2^-/\text{NO}_3^-$ meat curing salt for inhibition of *Cl. botulinum*. RM

20

[Nitrates, nitrites and nitrosamines.] Nitrate, Nitrite und Nitrosamine.

Liepe, H.-V.; Pfeil, E.

Fleischwirtschaft 59 (6) 826–830; 851 (1979) [De, en] [Fa. Rudolf Müller & Co., Giessener Strasse 94, 6301 Pohlheim 1, Federal Republic of Germany]

This review-type article discusses the role of nitrates, nitrites and nitrosamines in biological processes, and shows that their part in the natural N cycle makes it impossible to prevent their introduction into the diet. RM

21

Nitrosamines – a problem that concerns everyone.

Hofmann, K.

Fleischwirtschaft 59 (6) 823–825; 852–853 (1979) [En, De] [Schrotacker 19, 8650 Kulmbach, Federal Republic of Germany]

The problem of carcinogenic nitrosamines in food is discussed in a general context, i.e. exogenous and endogenous production, NO_3^- residues in food plants and drinking water, the antagonistic effect of ascorbic acid, and possible reduction of nitrite use in meat products. RM

22

Volatile nitrosamines in various cured meat products: effect of cooking and recent trends.

Sen, N. P.; Seaman, S.; Miles, W. F.

Journal of Agricultural and Food Chemistry 27 (6) 1354–1357 (1979) [26 ref. En] [Food Res. Div., Health Protection Branch, Ottawa, Canada K1A 0L2]

A study was carried out to determine the effect of cooking on levels of volatile nitrosamines in various cured meat products. Of 64 samples tested, 39 were negative (<0.1 parts/billion, p.p.b.) both before and

after cooking. The majority of the positive samples contained extremely low levels (<1 p.p.b.) of nitrosamines; the highest level detected was 8.6 p.p.b. *N*-nitrosopiperidine in a sample of spiced smoked beef. Only in 2 cases were significant increases in the levels of nitrosamines observed after cooking. 10 samples of baby foods containing various meat products were all found to be negative. In addition, 12 samples of fried bacon and 10 of cooked-out bacon fats were analysed; all were positive for *N*-nitrosopyrrolidine and *N*-nitrosodimethylamine, and in some cases *N*-nitrosodiethylamine. Results indicate a continuously lowering trend in the levels of volatile nitrosamines in all types of cured meat products, except fried bacon. AS

23

Starter culture reduces residual nitrite in bacon. Andres, C.

Food Processing 40 (5) 56-58 (1979) [1 ref. En]

The USDA has recently approved a process for the production of bacon which uses a starter culture of lactobacilli in the pickling solution to reduce formation of nitrosamines in the bacon at the time of frying. The effect depends on the culture reducing the pH of the meat, which reduces the amount of residual nitrite in the bacon. Both reduced nitrite levels and lower pH contribute to the minimization of formation of nitrosamines. Research has also shown that the cultures effectively prevent the formation of toxins in meat previously inoculated with *Clostridium botulinum* spores. A technique for predicting the nitrosamine content of bacon at 21 days after packaging on the basis of earlier analyses is also briefly described. JRR

24

The use of alpha-tocopherol in bacon processing. An update. [Lecture]

Mergens, W. J.; Newmark, H. L.

Proceedings of the Meat Industry Research Conference pp. 79-84 (1979) [13 ref. En] [Hoffmann-La Roche Inc., Nutley, New Jersey, USA]

The potential for use of α -tocopherol to block nitrosamine formation in the lipid phase during frying of bacon is discussed, with reference to literature data. Addition of α -tocopherol at 250-500 p.p.m. to bacon maintains the nitrosamine content of the fried product below current and proposed max. tolerance values in the USA. Studies on methods of application of α -tocopherol to bacon indicate that effective control of nitrosamine formation may be achieved by addition of tocopherol to the curing brine (with the addition of emulsifiers), or by spraying. Satisfactory protection against nitrosamine formation was observed even for bacon sprayed with tocopherol immediately before frying; uniform distribution of tocopherol in the rendered fat occurs before commencement of nitrosamine formation. The safety of α -tocopherol is discussed; it is suggested that the slightly increased dietary α -tocopherol intake resulting from this process might be advantageous. [See FSTA (1980) 12 5S714.] AJDW

25

Process control of bacon manufacture. [Lecture] Paul, D. L.

Proceedings of the Meat Industry Research Conference pp. 93-97 (1979) [En] [Ocar Mayer & Co., Madison, Wisconsin, USA]

General aspects of process control in bacon manufacture are discussed, with special reference to problems in relation to nitrosamines in the fried product. Aspects considered include: grading of pork bellies on the basis of wt.; trimming of the bellies to minimize differences in fat/lean ratio; prompt cooling and transport to the curing operation; curing by pickle injection to give a nitrite concn. of 120 p.p.m. and an ascorbate or erythorbate concn. of 550 p.p.m. in the belly; effects of draining time after injection on retention of curing brine in the product; standardization of curing brine composition; checking of the performance of brine-injection systems; maximization of uniformity of heat treatment in the smokehouse; optimization of wt. losses during curing; uniform chilling after smoking; and checking for nitrosamine formation in the finished product (analysis of slices fried at 340°F for 3 min/side). [See FSTA (1980) 12 5S714.] AJDW

26

The nitrite/*N*-nitrosamine problem in meats: an update. [Review]

Gray, J. I.; Randall, C. J.

Journal of Food Protection 42 (2) 168-179 (1979) [128 ref. En] [Dep. of Food Sci., Univ. of Guelph, Guelph, Ontario N1G 2W1, Canada]

Since certain *N*-nitrosamines are highly carcinogenic, formation and isolation of these compounds from food systems has received much attention in the past decade. This paper reviews the *N*-nitrosamine literature of the past 3 yr, especially as it relates to cured meat products. This review examines occurrence of nitrites and amines in food systems, presence of *N*-nitrosamines in bacon, and also means of minimizing formation of these compounds. In addition, regulatory changes pertaining to nitrite usage in curing procedures as well as some areas of future research are discussed. AS

27

A simple screening method for determination of volatile nitrosamines in fried bacon rasher and cook-out fat.

Cross, C. K.; Bharucha, K. R.

Journal of Agricultural and Food Chemistry 27 (6) 1358-1360 (1979) [8 ref. En] [Canada Packers Ltd., Toronto, Ontario, Canada M6N]

A method is described for rapid screening of cooked bacon rasher for volatile nitrosamines. The analysis is based on fluorescence densitometry of the nitrobenzooxadiazole amines produced by reaction of the amines liberated from nitrosamines by HBr in glacial acetic acid or preferably HBr in dichloromethane with 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl). The NBD amines are separated by TLC on silica gel. The limit of detection is in the order

of 1 µg/kg using a 20-g sample. The technique has been compared with a gas chromatograph-thermal energy analyzer method and showed excellent agreement. AS

28

Analysis of *N*-nitrosamines and nitramines in foods and herbicides.

Hotchkiss, J. H.

Dissertation Abstracts International, B 40 (2) 660-661; Order no. 79-17870, 147pp. (1979) [En] [Oregon State Univ., Corvallis, Oregon 97331, USA]

A method for detn. of volatile *N*-nitrosamines in foods and other environmental samples is described, based on vacuum distillation of the sample in mineral oil, extraction with dichloromethane, cleanup by acid and base extraction methods, concn. by solvent distillation, and GLC-thermal energy analysis. Extracts giving a positive response are subjected to further cleanup on activated alumina, re-concentrated, and injected into the GLC-thermal energy analyser system; peaks are trapped using a tube cooled in dry ice/methoxyethanol, and subsequently confirmed by GLC/low resolution MS. The method was demonstrated to be effective for *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine added to fried bacon, fried pork, raw fish or cheese at a concn. of 1 mg/kg; it was also employed to quantitate and confirm dimethylnitrosamine and *N*-nitrosopyrrolidine in fried commercial bacons at levels < 10 µg/kg. Further trials showed that various nitramines (which may occur in herbicides) gave false positive results for nitrosamines in thermal energy analysis; MS confirmation is therefore essential. High-resolution MS of the *m/e* 30 ion is unsuitable, as both nitramines and nitrosamines contain this ion. AJDW

29

[Nitrates, nitrites, nitrosamines and bacteria.] [Review]

Cantoni, C.; D'Aubert, S.; Perlasca, M.

Industrie Alimentari 18 (10) 741-745 (1979) [58 ref. It, en] [Istituto di Ispezione degli Alimenti di Origine Anim., Univ. degli Studi di Milano, Milan, Italy]

Bacterial synthesis of nitrates, nitrites and nitrosamines is reviewed, with particular reference to nitrite production by Enterobacteriaceae. AS

30

[Determination of *N*-nitrosamines in foods intended for long-term storage.]

Melamed, D. B.

Voprosy Pitaniya No. 5, 57-61 (1979) [15 ref. Ru, en] [Inst. Pitaniya AMN SSSR, Moscow, USSR]

Contents of *N*-nitrosamines (*N*-nitrosodimethylamine (NDMA), *N*-nitrosodiethylamine (NDEA) and *N*-nitrosopiperidine (NP)), were determined fluorometrically in 7-11 samples each of smoked sprat in oil, smoked mackerel in oil, silver hake in tomato sauce, krill in tomato sauce, Alaska pollock in tomato sauce, sprat in oil, and sprat pate. Except for the pollock, which contained only NDMA (0.8-3.0 µg/kg), all samples contained all 3 amines in mean concn.

(µg/kg) ranging from 2.0 to 9.0, 1.0 to 3.0 and 2.0 to 13.0 for NDMA, NDEA and NP, resp.; in all cases the highest concn. were found in the sprats in oil. Additionally, NDMA only was found in several other food products (prepared breakfast dish, fish soup, pickled beef, pickled pork, vegetable snack product, dried milk, dried egg, goulash) in mean concn. ranging from 1.0 to 3.0 (breakfast dish) µg/kg. No *N*-nitrosamines were found in samples of dried foods (prunes, apples, mushrooms), biscuits, various vegetable products (soy beans, green vetch) and food concentrates (beetroot soup with meat, fish soup, tomato sauce). It is concluded that although no direct correlation was established between the content of nitrosation agents in foods for long-term storage and *N*-nitrosamine formation, all possible steps should be taken to reduce the products nitrite content. HBr

31

N-nitrosamines. [Conference proceedings]

Anselme, J.-P. (United States of America, American Chemical Society, Division of Agricultural & Food Chemistry) (Editor)

ACS Symposium Series 101, x + 204pp. ISBN 0-8412-0503-5 (1979) [many ref. En] Washington DC, USA [Univ. of Massachusetts, Boston, Massachusetts, USA]

This book is based on papers presented at a symposium at the 8th Northeast Regional Meeting of the American Chemical Society, Boston, Massachusetts, on 25-28 June 1978. Many of the chapters deal with *N*-nitrosamine chemistry. Chapters of food interest are: Quantitative aspects of exposure and mechanism in *N*-nitrosamine carcinogenesis, by J. S. Wishnok (pp. 153-163, 34 ref.). *N*-nitrosamines as environmental carcinogens, by W. Lijinsky (pp. 165-173, 31 ref.). AL

32

Microbial degradation of nitrosamines. I. Inducible breakdown of nitrosamines.

Harada, K.; Yamada, K.

Bulletin of the Japanese Society of Scientific Fisheries [Nihon Suisan Gakkai-shi] 45 (7) 925-928 (1979) [19 ref. En] [Lab. of Biochem., Dep. of Food Sci. & Tech., Shimonoseki Univ. of Fisheries, Shimonoseki 759-65, Japan]

In order to investigate the microbial degradation of nitrosamines, the degrading activity of 3 strains of non-pathogenic microorganisms, i.e. *Rhizopus oryzae*, *Streptococcus cremoris*, and *Saccaromyces rouxii*, was examined. These microorganisms were active in degrading nitrosodimethylamine (NDMA), nitrosodiethylamine (NDEA), nitrosodipropylamine (NDPA), nitrosopyrrolidine (NPYR) and nitrosopiperidine (NPIP), NDPA being degraded more rapidly than the other nitrosamines. *R. oryzae* degraded 80% of NDPA, 40% of NPIP, 25% of NDEA, 20% of NPYR, and 10% of NDMA (% of amounts added to the medium). *S. cremoris* and *Sacc. rouxii* degraded 70% and 50% of NDPA resp.; the other nitrosamines were degraded to a smaller extent. NDPA was also degraded faster in the suspension of cells of these 3 strains precultured in the medium containing the nitrosamine than in the control cultures, i.e. suspensions of cells

harvested from the medium which did not contain NDPA. The cell-free extract of *R. oryzae* grown in the medium containing either NDMA or NDPA was active in degrading these 2 nitrosamines. These results suggest that the degradation of nitrosamines is conducted by an inducible enzyme. AS

33

Toxicological aspects of food safety - carcinogenicity and mutagenicity. [Lecture]

Preussmann, R.

Archives of Toxicology Suppl. 1, 69-84 (1978) [60 ref. En] [Deutsches Krebsforschungszentrum, Inst. für Toxikologie & Chemotherapie, D-6900 Heidelberg 1, Federal Republic of Germany]

Concepts of 'threshold' and 'safe level' for carcinogens such as nitrosamines in foods are discussed, as are correlations between carcinogenicity and results of mutagenicity tests. Carcinogens mentioned specifically include halogenated aliphatic compounds in drinking water, vinyl chloride in foods packaged in PVC, and *N*-nitroso compounds in meat and fish products and cheeses. Previously unpublished results of a survey of cheeses on the market in Germany showed low contents of *N*-nitrosamines; 20 samples of 168 examined contained nitrosamines at a max. level of 6 parts/billion. [See FSTA (1980) 12 7A448.] DIH

34

Formation of *N*-nitrosamines from Maillard browning reaction products in the presence of nitrite. Coughlin, J. R.

Dissertation Abstracts International, B 40 (2) 719: Order no. 79-17151, 344pp. (1979) [En] [Univ. of California, Davis, California 95616, USA]

Chemical studies and Ames *Salmonella*/microsome mutagenicity assays were conducted on potentially carcinogenic/mutagenic volatile and non-volatile *N*-nitroso compounds formed from Maillard reaction products in the presence of nitrite, particular attention being paid to the *N*-nitrosation of secondary amine Amadori compounds (*N*-substituted-1-amino-1-deoxy-2-ketoses). Ames assays indicated that *N*-nitrosated Amadori compounds can act as direct mutagens on *S. typhimurium*. Amadori compounds occur widely in browned heat-processed foods and beverages and it is suggested that these compounds may contribute to the causation of human gastro-intestinal tract cancer, either by ingestion of preformed compounds or by in vivo nitrosation of precursor Amadori compounds following ingestion. HPLC separation of Amadori compounds was achieved by using reversed-phase, ion-pairing chromatography and a bonded NH₂ column. Other chromatographic techniques were also used to study the Amadori compounds. Further studies included successful *N*-nitrosation in acidic NaNO₂ solution of the 1:1 D-glucose/L-cysteine condensation product containing the thiazolidine ring; the resulting β -oxidized *N*-nitrosamine is a potential carcinogen/mutagen which could readily form in nitrite-containing foods or by in vivo nitrosation of the condensation adduct in the gastro-intestinal tract. JA

35

Contamination of some fermented Nigerian beverages by carcinogenic nitrosamines.

Maduagwu, E. N.; Joaquim, K. A.; Bassir, O.

Tropical and Geographical Medicine 31 (2) 283-290 (1979) [31 ref. En] [Dep. of Biochem., Univ. of Ibadan, Ibadan, Nigeria]

A survey to determine the extent of the nitrosamine contamination of some popular fermented Nigerian beverages by dimethyl- and diethylnitrosamine was carried out in the Lagos, Ogun, Oyo, Ondo, Kwara and Benue States of Nigeria, following the MS detection of these carcinogens in palm-wine and nono (sour milk). The indication is that the contamination of the drinks, i.e. palm-wine, nono, pito, burukutu and ogogoro, by both nitrosamines was widespread and occurred at the part/billion level. 0.6-22 μ g nitrosamine/l was found by routine TLC and GLC methods using authentic nitrosamines as reference standards. Because of the widespread contamination of the test beverages by dimethyl- and diethylnitrosamine, and the usually frequent occurrence of nitrosamine precursors in nature, it is presumed that these potent and versatile carcinogens could play a significant role in the formation of human cancers in the Nigerian population. AS

36

Confirmation of low μ g/kg amounts of volatile *N*-nitrosamines in foods by low resolution mass spectrometry.

Hotchkiss, J. H.; Libbey, L. M.; Scanlan, R. A.

Journal of the Association of Official Analytical Chemists 63 (1) 74-79 (1980) [13 ref. En] [Dep. of Food Sci., Oregon State Univ., Corvallis, Oregon 97331, USA]

Volatile *N*-nitrosamines were confirmed in foods at concn. of < 10 μ g/kg by full scan low resolution MS. Ground samples were vacuum-distilled from mineral oil and condensed in liquid N₂-cooled vapour traps. The thawed distillate was extracted, the extract was cleaned up and concentrated, and *N*-nitrosamine content was determined by combined GLC-thermal energy analysis. Positive samples were further cleaned up, trapped from a gas chromatographic column, and purged into a gas chromatograph-mass spectrometer for qualitative confirmation by full scan low resolution MS. This procedure was applied to foods spiked at 1 μ g/kg and to fried commercial bacons with volatile *N*-nitrosamine contents of 2-5 μ g/kg. AS

37

Precooked bacon offers higher yields, better flavor, reduced nitrosamines.

Anon.

Food Product Development 13 (10) 34, 36 (1979) [En]

Westland Foods of Concord, California produce cool-cooked bacon, a product precooked by microwaves during processing. Cool-cooking is an in-plant combination of microwave and conventional heating that cooks the product throughout without raising the temp. in any portion to > 240°F. With current 120 p.p.m. nitrite bacon the process forms almost no nitrosamines. Fewer volatiles are driven off

and aroma and flavour are better, as are fat stability and colour. Strips do not shrink as much, distort, burn or speckle. Cool-cooked bacon, at a yield of 20–25 slices/lb, looks about the same on a plate as regular 16–18 count bacon. In other words, 10–30% less raw bacon produces the same end result. Cool cooked sandwich bacon is 35 count. Processing utilizes an industrial-sized microwave unit with two 25 kW magnetrons used in conjunction with conventional heating. 2 heating systems have been used successfully – one employs microwaves and hot air simultaneously; the other uses steam, hot air and finally microwaves. Generally the precooked product is down to 30% of its starting wt. The precooked bacon is generally shipped frozen. To serve, the bacon is broiled for 60 s or grilled for 90 s. It can be cooked in a 400°F oven for 1½–2 min. Cool-cooked bacon promises to alleviate the nitrosamine problem and offers costs savings by increasing yields up to 30%, improving shelf life and improving bacon flavour and aroma on the consumer's plate. VJG

38

Effect of processing on the amino acid composition and nitrosamine formation in pork belly adipose tissue.

Spinelli-Gugger, A. M.; Lakritz, L.; Wasserman, A. E. *Journal of Agricultural and Food Chemistry* 28 (2) 424–427 (1980) [21 ref. En] [E. Reg. Res. Cent., USDA, Philadelphia, Pennsylvania 19118, USA]

The curing process does not alter the concn. of free amino acids in the adipose tissue of pork bellies. Frying of the adipose tissue leads to a decrease in the level of free amino acids; greater reductions were seen in the processed vs. untreated tissue. Analysis for nitrosamines in the fried samples indicate that dimethylnitrosamine and nitrosopyrrolidine formation is independent of free amino acid concn. A study of the lean, adipose and intact tissue of country cured bacon indicates that frying generates up to a tenfold increase in free amino acids in the lean and intact tissue, while comparatively negligible changes are noted in the adipose. AS

39

[Determination of volatile nitrosamines in foods of animal origin.] Beitrag zur Analytik flüchtiger Nitrosamine in tierischen Lebensmitteln.

Fritz, W.; Uhde, W.-J.

Nahrung 24 (4/5) 471–477 (1980) [18 ref. De, en, ru] [Zentralinst. für Ernährung, Potsdam-Rehbrücke, German Democratic Republic]

A procedure for detn. of volatile *N*-nitrosamines in foods of animal origin is described. Nitrosamines are isolated from the food sample by vacuum distillation, and extracted from the distillate (acidified to pH 1 with H₂SO₄) by means of methylene chloride. The nitrosamines are then denitrosated (by HBr treatment) to the corresponding amines; the amines are derivatized with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole. The resulting fluorescent amine derivatives are then separated by 2-dimensional TLC on silica gel G plates, using benzene/diethyl ether/toluene (7:2:1) and *n*-heptane/ethyl acetate/*n*-butanol (8:1:1) solvent

systems. The amines are determined in situ on the TLC plate by fluorescence spectrophotometry (excitation at 360 nm, emission at 526 nm). Recovery of 4 nitrosamines from pork and fish ranged from 40 to 90%. Detection limit is 0.1 µg/kg. IN

40

[Formation of *N*-nitroso compounds in foods.] Zur Bildung von *N*-Nitrosoverbindungen in Lebensmitteln. [Review]

Fritz, W.; Uhde, W.-J.

Ernährungsforschung 24 (6) 181–184 (1979) [39 ref. De] [Zentralinst. für Ernährung, Potsdam-Rehbrücke, German Democratic Republic]

Aspects considered include: non-carcinogenic precursors in foods; amino groups susceptible to nitrosation; formation of *N*-nitroso compounds in foods of animal and vegetable origin; occurrence of *N*-nitroso compounds in foods and in drinking water; nitrosating agents; formation of *N*-nitroso compounds in foods as a result of processing (smoking, roasting) or microbial action; transfer of nitrosamines from feed (e.g. fish meal, silage) into foods of animal origin; and the effects of nitrosated pesticides and excessive levels of N fertilization on nitrosamine concn. in foods. IN

41

Nitrosamines in alcoholic beverages.

Sen, N. P.; Seaman, S.; McPherson, M.

Journal of Food Safety 2 (1) 13–18 (1980) [11 ref. En] [Food Res. Div., Food Directorate, Health Protection Branch, Ottawa, Canada K1A 0L2]

A limited survey was carried out to determine the nitrosamine content of several var. of alcoholic beverages (beer and ale, whiskey, wine, cider, etc.) sold in Canada. Of 22 samples of different beers and ales analysed all but 1 contained traces of dimethylnitrosamine; the overall mean level found was 1.5 parts/billion. Only 1 Canadian rye and 1 Scotch whiskey out of a total of 13 samples contained traces of either dimethylnitrosamine or diethylnitrosamine. All the 8 wines and 7 cider samples were negative. AS

42

Analysis of volatile *N*-nitrosamines in alcoholic beverages.

Goff, E. U.; Fine, D. H.

Food and Cosmetics Toxicology 17 (6) 569–573 (1979) [24 ref. En] [New England Inst. for Life Sci., 125 Second Avenue, Waltham, Massachusetts 02154, USA]

A description is given of a simplified analytical technique for analysis of volatile *N*-nitrosamines in alcoholic beverages, which involves a single step liquid-liquid extraction on a Preptube using dichloromethane, followed by concn. of the eluate and analysis by GLC-Thermal Energy Analyser. The method, sensitive at the 0.2 mg/l level for *N*-nitrosodimethylamine (NDMA), was applied to alcoholic beverages purchased from liquor stores in Massachusetts and at state liquor stores in New Hampshire. Recovery studies were conducted by spiking the liquor samples with 5 mg/l of each of 7 *N*-nitrosamines. Range of recoveries and detection limits are tabulated for the nitrosamines in the spiked

liquor samples. Volatile nitrosamines were not found in any of the wines (19 samples), sherries (3), liqueurs (4), gin (3), vodka (3) and rum (3). All 18 brands of domestic and imported beer contained NDMA at levels ranging from 0.4 to 7.0 mg/l and 6 of the 7 brands of Scotch whisky also contained NDMA at levels between 0.3 and 2.0 mg/l. VJG

43

N-nitrosamides and their precursors in food systems. I. Formation of N-substituted amides.

Kakuda, Y.; Gray, J. I.

Journal of Agricultural and Food Chemistry 28 (3) 580-584 (1980) [14 ref. En] [Dep. of Food Sci., Univ. of Guelph, Guelph, Ontario N1G 2W1, Canada]

A study was conducted to establish the formation of N-substituted amides from primary amino compounds (α -amino acids and primary amines) and fatty acids or their esters under conditions involving thermal stress. Results indicate that fatty acid esters and free amines react readily to form such amides. Free fatty acids are not as reactive as their respective triglycerides, but at high temp. both react readily with amines. The formation of primary amines via the decarboxylation of α -amino acids appears to be unlikely under normal cooking conditions (e.g. oven roasting of pork or pan-frying of bacon) due to insufficient energy for the decarboxylation reaction. High temp. (min. 150°C for 45 min) were required for the decarboxylation of norleucine. It was concluded that under the conditions encountered in the processing and cooking of foods, only amines would react with fatty acids (or esters) to yield substantial quantities of secondary amides. [See following abstr. for part II.] AS

44

N-nitrosamides and their precursors in food systems. II. Kinetics of the N-nitrosation reaction.

Kakuda, Y.; Gray, J. I.

Journal of Agricultural and Food Chemistry 28 (3) 584-587 (1980) [17 ref. En] [Dep. of Food Sci., Univ. of Guelph, Guelph, Ontario N1G 2W1, Canada]

The N-nitrosation reaction between NaNO_2 and N-substituted amides formed from the interaction of amines and fatty acids or triglycerides was studied as a function of pH and temp. There was no apparent pH max. for the reaction, N-nitrosamide formation increasing with increasing H^+ concn. The rates of N-nitrosation decreased rapidly as the pH increased and little reaction occurred $> \text{pH } 3$. A unit drop in pH from 2 to 1 increased the rate of N-nitrosation by a factor of 5-8 times. The rate constants for the reaction remained relatively constant over the pH range 1-3.5, supporting the nitrous acidium ion mechanism. When the temp. of the reaction was increased to 40°C, the rate constants were almost double those determined at 30°C, indicating an activation energy of approx. 10 kcal/mol. The rate constants again remained relatively constant as the initial amide and nitrite concn. were varied between 20 and 40 mM. [See preceding abstr. for part I and following abstr. for part III.] AS

45

N-nitrosamides and their precursors in food systems. III. Influence of pH and temperature on stability of N-nitrosamides.

Kakuda, Y.; Gray, J. I.; Lee, M.-L.

Journal of Agricultural and Food Chemistry 28 (3) 588-591 (1980) [11 ref. En] [Dep. of Food Sci., Univ. of Guelph, Guelph, Ontario N1G 2W1, Canada]

The decomposition of N-nitrosamides was investigated in aqueous and organic solvents as a function of temp. and pH. In aqueous solvent, N-nitrosomethylpropionamide (NOMP) had max. stability at pH 4.0 over the temp. range 4-50°C. Further experiments also confirmed that N-nitrosamides are much less stable than volatile N-nitrosamines such as N-nitrosopyrrolidine (N-Pyr) and dimethylnitrosamine (DMN). Thermal decomposition studies utilizing heating conditions commonly encountered in the pan frying of bacon and oven roasting of pork indicated that NOMP was degraded to the extent of 74-97% compared to 3-14% for N-Pyr and DMN. It was tentatively concluded that the major contribution of N-substituted amides, if present in foods, may be as precursors of N-nitroso compounds formed by in vivo N-nitrosation reactions. [See preceding abstr. for part II.] AS

46

Overview of some aspects of occurrence, formation and analysis of nitrosamines.

Fishbein, L.

Science of the Total Environment 13 (3) 157-188 (1979) [177 ref. En] [US Dep. Health, Education & Welfare, FDA, Nat. Cent. for Toxicology Res., Jefferson, Arkansas 72079, USA]

This review principally addresses a number of aspects of the occurrence and formation of the nitrosamines, highlighting principal areas of potential concern ranging from the spectrum of nitrosatable moieties found in the environment (e.g., secondary and tertiary amines, quaternary ammonium compounds, ureas, carbamates and guanidines), specific examples of nitrosamines found in food, alcoholic beverages, feed (and their significance for carcinogenesis bioassays), air and water. The factors influencing in vitro and in vivo nitrosation and the evidence for the latter in man are also discussed. Additionally, germane areas of the analysis of nitrosamines are reviewed with a focus on the major areas of concern and requirements of extreme sensitivity and selectivity in addition to the problems of artifacts in the analytical procedures. AS

47

N-Nitrosodimethylamine in beer.

Scanlan, R. A.; Barbour, J. F.; Hotchkiss, J. H.; Libbey, L. M.

Food and Cosmetics Toxicology 18 (1) 27-29 (1980) [11 ref. En] [Dep. of Food Sci. & Tech., Oregon State Univ., Corvallis, Oregon 97331, USA]

25 samples of canned or bottled beers produced in the USA were purchased at local retail outlets. Volatile

nitrosamines were extracted from the samples by a distillation procedure and determined using a chemiluminescence detector. *N*-Nitrosodimethylamine (NDMA), the only volatile nitrosamine found, was detected in 23 of 25 samples analysed. Mean and range for NDMA (parts/billion) with number of samples in parentheses for the different types of USA beer are: Pilsen lager (15), 7.7, 0-14; low calorie lager (3), 4.0, 0-7; ale (2), 5, 3-7; dark lager (2), 0.7, 0.5-0.8; and malt liquor (3), 2.8, 0.5-5. The overall mean for all samples was 5.9 parts/billion NDMA and the range was 0-14 parts/billion. The identity of NDMA was confirmed by MS. VJG

48

Analysis of malted barley for *N*-nitrosodimethylamine.

Hotchkiss, J. H.; Barbour, J. F.; Scanlan, R. A. *Journal of Agricultural and Food Chemistry* 28 (3) 678-680 (1980) [11 ref. En] [Dep. of Food Sci. & Tech., Oregon State Univ., Corvallis, Oregon 97330, USA]
4 procedures for isolation of *N*-nitrosodimethylamine (NDMA) from direct-fired kiln dried malted barley were compared: Soxhlet extraction with dichloromethane, direct aqueous extraction, steam distillation, and vacuum distillation. A gas chromatograph coupled to a thermal energy analyser was used to estimate levels of NDMA. All the isolation procedures gave similar results with the exception of the Soxhlet extraction which gave 1/4 the NDMA content of the other 3 methods. Grinding the malt did not significantly affect the level of NDMA. It was also determined that, without addition of approx. 70% of the sample wt. in water, the NDMA concn. found by vacuum distillation was significantly reduced. AS

49

[Effect of additives on nitrosamine formation in bacon.] Beeinflussung der Nitrosaminbildung in Bacon durch Zusatzstoffe.

Hauser, E.; Heiz, G. J. *Archiv für Lebensmittelhygiene* 31 (2) 43-45 (1980) [13 ref. De, en] [Bundesamt für Veterinärwesen, Bern, Switzerland]

The formation of dimethylnitrosamine (DMNA) and nitrosopyrrolidine (NPY) in fried bacon and bacon fat was reduced, by addition of ascorbate (200 p.p.m. sodium ascorbate + 200 p.p.m. ascorbyl palmitate), to 3-8 parts/billion (which escaped partly in the steam from frying). RM

50

[Problems with formation of *N*-nitroso compound precursors as a result of fumigation of foods with alkylating agents. I. Investigation on formation of secondary amines by the action of ethylene oxide on primary amines and amino acids.] Zur Problematik der Anwendung alkylierender Substanzen bei der Lebensmittelbegasung hinsichtlich der Bildung von Vorstufen der *N*-Nitrosoverbindungen. I. Untersuchungen zur Bildung sekundärer Amine durch Einwirkung von Äthylenoxid auf primäre Amine und Aminosäuren.

Dunkelberg, H.

Zentralblatt für Bakteriologie, 1B 171 (1) 42-47 (1980) [12 ref. De, en] [Hygiene-Inst., Univ., Mainz, Federal Republic of Germany]

Studies on formation of secondary amines by reaction of ethylene oxide (EO) with primary amines, or by reaction of EO with amino acids followed by decarboxylation, are described. Reaction of EO with (i) methylamine, (ii) ethylamine, (iii) ethanolamine, (iv) glycine and (v) serine was investigated in model solutions; reaction products were analysed by TLC. The results show that methylaminoethanol, ethylaminoethanol and diethanolamine are formed from (i), (ii) and (iii) resp. EO treatment of (iv) and (v) at pH > 8 followed by decarboxylation gave low yields of methylaminoethanol and diethanolamine. Reaction of EO with (iv) or (v) at lower pH failed to yield these reaction products. AJDW

51

[Problems with formation of *N*-nitroso compound precursors as a result of fumigation of foods with alkylating agents. II. *N*-methylation of various amino acids by the action of methyl bromide.] Zur Problematik der Anwendung alkylierender Substanzen bei der Lebensmittelbegasung hinsichtlich der Bildung von Vorstufen der *N*-Nitrosoverbindungen. II. *N*-Methylierung verschiedener Aminosäuren durch Einwirkung von Methylbromid. Dunkelberg, H.

Zentralblatt für Bakteriologie, 1B 171 (1) 48-54 (1980) [9 ref. De, en] [Hygiene-Inst., Univ., Mainz, Federal Republic of Germany]

Studies were conducted on *N*-methylation of the amino acids (i) glycine (ii) alanine, (iii) valine, (iv) leucine and (v) glutamic acid (in aqueous solutions) by liquid methyl bromide at pH 7, 8 or 10, reaction times of 1, 2, 3, 4 and 8 h being evaluated. Reaction products were separated and identified by TLC. The results show formation of the appropriate *N*-methyl derivatives of (i)-(v). Reaction rate and *N*-methyl derivative yield increased with increasing pH. There was a tendency for *N*-methyl derivative yield to decrease from 3-4 h reaction time up to 8 h reaction time. [See preceding abstr. for part I.] AJDW

52

Evaluation of the carcinogenic risk of chemicals to humans. Some *N*-nitroso compounds.

International Agency for Research on Cancer; World Health Organization
IARC Monographs 17, 365pp. ISBN 92-832-12177 (1978) [many ref. En] Lyon, France. Price £17.50; FS50.00; \$25.00 [Obtainable from HMSO Books (PM1C), Atlantic House, Holborn Viaduct, London EC1P 1BN, UK]

This publication represents the views and expert opinions of an IARC Working Group which met in Lyon, France, on 10-15 Oct. 1977. The preamble (pp. 11-34, 77 ref.) deals with background, objective and scope, selection of chemicals for monographs, working procedures, data for evaluations, the working group, general principles for evaluating the carcinogenic risk of chemicals, and explanatory notes on the monograph

contents. General remarks are given on the substances considered (pp. 35-47, 79 ref.). The monographs cover chemical and physical data, production, use, occurrence and analysis, biological data relevant to the evaluation of carcinogenic risk to man, summary of data reported and evaluation, and references for the following chemicals of possible food interest: *N*-Nitrosodi-*n*-butylamine (pp. 51-75); *N*-Nitrosodiethylamine (pp. 83-124); *N*-Nitrosodimethylamine (pp. 125-175); *N*-Nitrosodi-*n*-propylamine (pp. 177-189); *N*-Nitroso-*N*-ethylurea (pp. 191-215); *N*-Nitrosomethylethylamine (pp. 221-226); *N*-Nitrosomethylvinylamine (pp. 257-261); *N*-Nitrosopiperidine (pp. 287-301); *N*-Nitrosoproline and *N*-nitrosohydroxyproline (pp. 303-311); *N*-Nitrosopyrrolidine (pp. 313-326); and *N*-Nitrososarcosine (pp. 327-335). A cumulative index to IARC Monographs of chemicals studied is included (pp. 353-365). AL

53

Plant uptake of dinitroaniline herbicide-related nitrosamines.

Kearney, P. C.; Oliver, J. E.; Kontson, A.; Fiddler, W.; Pensabene, J. W.

Journal of Agricultural and Food Chemistry 28 (3) 633-635 (1980) [8 ref. En] [Pesticide Degradation Lab., USDA, Beltsville, Maryland 20705, USA]

As *N*-nitrosodipropylamine (NDPA) and *N*-nitrosopendimethalin (NP) have been reported as contaminants of the commercial herbicides trifluralin and pendimethalin, resp., possible human exposure to these nitrosamines was assessed by growing soybeans in soils containing various concn. of ^{14}C -labelled NDPA or NP. Soil concn. used in pot experiments were 0-100 parts/billion NDPA or NP, corresponding at the highest level to $> 300\times$ those encountered by normal use of the corresponding herbicides. Soils and plant parts were analysed for nitrosamines by ^{14}C analysis (combustion, extraction and steam distillation analysis all used), and by GLC-thermal energy analysis (GLC-TA); limits of detection were 0.01-1 ng/g for ^{14}C analysis and 0.35 ng/g for GLC-TA. Neither NDPA or NP was detected in soybeans grown on any of the soils, and ^{14}C residues from NDPA were not detected in upper plant parts. ^{14}C residues from NP were detected in upper plant parts other than beans, but were not identified as NP by TLC. DIH

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51. Meat Canning			

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